MAGNETIC STRUCTURES OF NANOMETER SCALE DY, CR AND NI*

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ANL/MSD/CP--77654

DE93 002984

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October 1992

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Received by OSTI

NOV 16 1992

Presented at the First International Conference on Nanostructured Materials in Cancun, Mexico from September 21-25, 1992.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contracts W-31-109-Eng-38 and W-7504-Eng-36. Additional support was provided by the German Federal Ministry for Research and Technology (BMFT) under contract number 03PE1LMU/2.

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Introduction

Materials composed of nanometer-sized structures are becoming technologically relevant as the sizes of electronic devices approach the nanometer scale. Questions as to the performance and durability of these devices can be partially addressed through the characterization and understanding of the magnetic structures and properties of nanometer-sized materials. The purpose of the present work is to understand the relationship between the microstructure of nanocrystalline materials and their magnetic structures and properties. This paper summarizes three separate experiments: (1) an X-ray diffraction and anomalous absorption (XANES) study of nanocrystalline Dy, (2) neutron diffraction measurements of the magnetic structure of nanocrystalline Cr, and (3) the measurement of the magnetization density of a single twist grain boundary in Ni.

Results and Discussion

The Micro- and Electronic Structures of Nanocrystalline Dy

Since rare earth elements typically have large magnetic moments and anisotropies, the nanocrystalline forms of these materials are expected to exhibit unusual magnetic properties. The present work involves the study of nanocrystalline Dy with X-ray diffraction and anomalous X-ray absorption. X-ray diffraction provides information about the microstructure of a material, and the absorption of X-rays near the L_{III} edge of Dy, provides information about the electronic structure of the bound atom. These measurements were made from a coarse-grained (c.g.) Dy foil specimen, and compacted and uncompactd nanocrystalline (5-35nm grain sizes) Dy specimens fabricated using the gas condensation method (1).

Measurements of the a_0 and c_0 lattice parameters taken as a function of temperature are shown in Figs. 1 and 2, respectively. The lattice parameters of both samples show normal (positive) thermal expansion in the paramagnetic region where $T > T_N = 179K$. In the antiferromagnetic region, where $T_C (= 86K) < T < T_N$, both parameters of the coarse-grained specimen decrease (contract) as temperature increases in a manner like that of single crystal Dy (2,3). In the ferromagnetic region ($T < T_C$), the a_0 parameter from the coarse-grained specimen, and the c_0 parameters of both specimens exhibit little thermal expansion or contraction, also like those of single crystal Dy (2,3). In contrast to these observations, the general expansion of the a_0 parameter of the nanocrystalline specimen at all temperatures is strikingly different than that of the coarse-grained sample, and is more similar to the behavior of the a_0 parameter in Ho than in Dy (3). Since the unusual thermal behaviors of the a_0 and c_0 parameters of coarse-grained and single crystal Dy are related to the coupling between the $4f$ electron orbitals and the crystal-field of Dy, a change in this behavior suggests that the coupling between the orbitals and the crystals in the compacted nanocrystalline material has changed, and may be more akin to the coupling which exists in Ho than normally observed in Dy.

Fig. 1 The a_0 lattice parameters of c.g. Dy (●) and compacted nanocrystalline Dy (○) versus temperature.

Fig. 2 The c_0 lattice parameters of c.g. Dy (●) and compacted nanocrystalline Dy (○) versus temperature.

Fig. 3 The X-ray absorption at the L_{III} edges of c.g. Dy and nanocrystalline Dy.

Fig. 4 The relative microstrain broadening of three Dy samples versus temperature.

This conclusion is further motivated by the observation of a shift of the L_{III} absorption edge in compacted nanocrystalline Dy compared to that of the coarse-grained material (Fig. 3). Since the position of the L_{III} edge is related to the valence of the atom, a 3eV shift to lower energy suggests that the outer orbitals, e.g. the $4f$ (magnetic), orbitals, are more tightly bound to the nucleus of an atom in nanocrystalline Dy than in the coarse-grained or single crystal material. If this conclusion is correct, then a change in the coupling behavior of these orbitals to the crystal-field is expected, which may be manifested as a change in the thermal behavior of the lattice parameters.

In addition to the potential change in the crystal-field coupling, the microstrain in the compacted nanocrystalline specimen is considerably larger than in either the coarse-grained or uncompact nanocrystalline specimens. The microstrain relative to that measured at room temperature, $\epsilon(T)/\epsilon(300)$, is plotted versus temperature in Fig. 4. Since the orientations of the magnetic moments of the nanocrystalline grains in the uncompact specimen are not constrained, the grains are free to align their magnetic moments parallel to the applied magnetic field of 1.2kG; thus, microstrain broadening of the diffraction peaks, which is caused by dislocations and/or planar defects like grain boundaries (4), is

not expected to be present in the diffraction pattern of this sample. Likewise, little microstrain broadening is expected from the coarse-grained material since the magnetoanisotropy of this material will be accommodated by the growth of preferred magnetic domains within each grain. If due to their small size nanocrystalline grains are monodomained, then the minimization of magnetic free energy, which results when the magnetic moment of a grain is aligned parallel to the applied field, will be counterbalanced by an increase of free energy caused by the introduction of shear stresses in or around the grain boundaries, which constrain the realignment of the grain. These shear stresses should produce additional strain broadening of the diffraction peaks (4); thus, an increase of the strain broadening component is expected when the specimen becomes ferromagnetic, like that observed in Fig. 4.

The Magnetic Structures of Nanocrystalline Cr

The magnetic structures of Cr have been widely studied because Cr is the classical example of an itinerant antiferromagnet, which at certain temperatures is characterized by an incommensurate spin-density wave (SDW) (5). Single crystal Cr exhibits three different magnetic phases, which are: paramagnetic when $T > T_N$ (311K), antiferromagnetic (AF_1) with a transverse SDW propagating in the [100] direction when T_{SF} (123K) $< T < T_N$, and antiferromagnetic (AF_2) with a longitudinal SDW also propagating in the [100] direction when $T < T_{SF}$ (6). In the polycrystalline form, Cr exhibits a combination of these magnetic structures, and a fourth magnetic phase—a simple commensurate antiferromagnetic (AF_0) phase (7,8). Bacon and Cowlam (7) have shown that strained polycrystalline Cr can exist in the AF_0 phase when $T_{SF} < T < T_N = 473K$, and is mostly in the AF_1 phase below T_{SF} . Bacon and Cowlam have also shown that the frequency of occurrence of the different phases can be greatly changed by high temperature annealing of the materials. The observation of strain dependent antiferromagnetism, also called technical antiferromagnetism (5), has motivated the present study of the magnetic structures of nanocrystalline Cr, which like other nanocrystalline materials has a severely strained microstructure (9).

The 1g sample examined in the present work was composed of forty disks of compacted nanocrystalline Cr powder made using the gas condensation technique (1). Chemical analysis of a representative disk showed that the primary impurity in the sample consisted of ~ 7 wt.% oxygen and ~ 1 wt.% water. The magnetic structures of this sample, and a 10g sample composed of 99.99% pure coarse-grained Cr chips, were deduced from neutron diffraction measurements made with the high intensity powder diffractometer at the Los Alamos Neutron Scattering Center (LANSCE). Portions of the diffraction patterns from the coarse-grained and nanocrystalline samples are shown in Figs. 5 and 6, respectively, for the temperatures of 19K and 323K.

The data from the coarse-grained sample taken at 19K is characterized by a central peak located at the (100) position in reciprocal space (corresponding to a forbidden nuclear reflection, but which is an allowed antiferromagnetic reflection) and two satellite reflections (marked by arrows in Fig. 5) displaced from the central reflection by $0.094\text{\AA}^{-1}$. These intensity peaks were not observed in X-ray diffraction measurements of the same sample, which are insensitive to magnetism; therefore, the intensity peaks in Fig. 5 are likely to have a magnetic origin. The magnitude of the SDW wavevector corresponding to this

Fig. 5 A portion of the c.g. Cr neutron diffraction pattern at two temperatures.

Fig. 6 A portion of the nano-Cr neutron diffraction pattern at two temperatures.

displacement is $Q_{SDW} = 2.09 \text{ \AA}^{-1}$, which is in good agreement with the published value of $2.07 \text{ \AA}^{-1}$ for the AF_1 phase (10). At a temperature of 323K, a strong intensity peak at the location of the (100) reflection is observed, which is consistent with either an AF_0 or AF_2 phase of Cr, although previous works (7,8) have attributed this intensity peak to the AF_0 phase. The observation of magnetic ordering above 311K in polycrystalline Cr has also been observed elsewhere (7), and suggests that T_N for the coarse-grained sample is increased compared to the literature value for single crystal Cr. This increase is an example of technical antiferromagnetism, since strain is known to change the magnetic structure of Cr (7,8), and significant strain (7×10^{-3}) was observed in the coarse-grained sample from the strain broadening of the nuclear Bragg reflections.

The diffraction measurements from the nanocrystalline Cr sample (Fig. 6) differ from those of the coarse-grained sample (Fig. 5) in four significant aspects. First the measurement taken at 19K from the nanocrystalline sample shows a primary reflection which is more intense than the central peak in Fig. 5, and two satellite reflections (whose existence is inconclusive), which are exceedingly weak compared to the intensities of the satellite reflections in Fig. 5. Secondly, the strong peak of intensity in Fig. 6 (which like the peaks in Fig. 5 was not observed with X-ray diffraction) is shifted from a position corresponding to the (100) reflection to a position nearly coincident with the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ location in reciprocal space. These observations can be explained by an antiferromagnetic structure with a magnetic stacking sequence of $++--++--$, where $+$ and $-$ denote opposite alignments of the magnetic moments of atoms in the atomic planes normal to the $[111]$ direction. Thirdly, no evidence for a magnetic reflection is seen from the nanocrystalline specimen at 323K. The lack of a magnetic reflection suggests that nanocrystalline Cr is paramagnetic at 323K unlike the coarse-grained sample, which is still antiferromagnetic at this temperature. Finally, the background in Fig. 5 is about five times less than that in Fig. 6, although the X-ray background in the former was only one-half that of the latter. This observation suggests that most of the additional background scattered by the nanocrystalline sample is from a source to which neutrons are more strongly coupled than X-rays, e.g. incoherent scattering from impurities containing oxygen and/or hydrogen.

Fig. 7 The reflectivity of unpolarized neutrons from a Ni bicrystal containing a large area [001] high angle twist grain boundary.

Fig. 8 The reflectivities of polarized neutrons with spin states parallel (R_+) and anti-parallel (R_-) to the magnetic field applied to the specimen in Fig. 7.

The Magnetic Structure of a [001] Ni Twist Grain Boundary

In the earlier two sections, experimental observations of changes in the nuclear and magnetic structures of nanocrystalline materials compared to those of the bulk have been reported. The origin of these changes remains unclear, since strain, impurities, finite particle size and grain boundary effects may all alter the magnetic structures of materials. In order to determine whether the latter can affect the magnetic behavior of polycrystals, an experiment was designed to measure the magnetic structure of a specific grain boundary. The experiment involved making polarized neutron reflection (PNR) measurements of a large area (9cm²) [001] high angle twist grain boundary in a Ni bicrystal. The bicrystal was manufactured by hot-pressing together two single crystals of Ni. One of the single crystals was epitaxially grown on a single crystal of MgO, while the other was epitaxially grown on a single crystal of NaCl from a mixture of Ni and ⁶²Ni. The mixture of Ni and ⁶²Ni was chosen so that the neutron scattering length of the Ni thin film was zero. After sintering the bicrystal together, the NaCl was dissolved leaving the Ni bicrystal attached to the MgO. By matching the neutron scattering length of the upper half of the bicrystal to that of vacuum, the grain boundary interface can be directly observed with neutron reflection.

The reflectivity of unpolarized neutrons versus momentum transfer perpendicular to the grain boundary interface is shown in Fig. 7. The reflectivity is related to the Fourier transform of the nuclear density gradient of the bicrystal, averaged over its lateral dimensions. Since the upper half of the bicrystal is transparent to neutrons, the density profile is similar to a combination of two step functions—one located at the grain boundary interface and the second at the Ni/MgO phase boundary. Such a density profile will provide many of the features seen in the reflectivity profile, e.g. the oscillations in Fig. 7; however, good agreement between the calculated and observed reflectivity profiles requires a modification of the first step function to account for the width and density of the grain boundary.

The reflectivities of neutrons with spins polarized parallel (R_+) and anti-parallel (R_-) to the magnetization of the Ni bicrystal are shown in Fig. 8. The splitting of the two

reflectivity curves is caused by the difference between the scattering potentials of the two neutron spin states. This splitting can be represented by a variation of the magnetization density profile of the bicrystal as a function of depth. As in the case of the unpolarized measurement where the nuclear density profile of a grain boundary can be deduced, the magnetization density profile of a single grain boundary can be deduced from the PNR measurements in Fig. 8.

General Conclusions

The magnetic properties and structures of materials manufactured from nanometer-sized grains are very different from those found in the bulk. These differences include: (1) changes in the magnetically regulated thermal expansion of nanocrystalline Dy, (2) ferromagnetically induced strain in nanocrystalline Dy, (3) a new magnetic structure for AF nanocrystalline Cr, and a change of T_N in nanocrystalline Cr. Since the magnetic properties of other polycrystals have been characterized in terms of their crystallite size, strain and impurity contents, these characteristics, which are found at the extremes in nanocrystalline materials, may be responsible for the unique magnetic properties of nanocrystalline materials. Alternatively, the magnetic properties of these materials may be determined by unique properties of grain boundaries, which are found in abundance in nanocrystalline materials; therefore, further studies of the magnetic structures of grain boundaries, like the one reported in this work, are required to understand and engineer materials composed of nanometer-sized particles.

Acknowledgments

This work was supported by the U.S. Department of Energy, BES-DMS, under contracts W-31-109-ENG-38 and W-7405-ENG-36. The research was partly carried out at the National Synchrotron Light Source (beamline X14A), Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. The Manuel Lujan Jr., Neutron Scattering Center is a national user facility funded by the U.S. Department of Energy, Office of Basic Energy Science. Additional support was provided by the German Federal Ministry for Research and Technology (BMFT) under contract number 03PE1LMU/2. We thank Dr. P. Zschack for his assistance with the use of NSLS beamline X14A.

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